Regular article

Generalized Christoffel–Darboux formulae and the frontier Kohn–Sham molecular orbitals

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Abstract. The Christoffel–Darboux formula for classical orthogonal polynomials is generalized to arbitrary sets of orthogonal functions in three dimensions, yielding an explicit link between frontier Kohn–Sham molecular orbitals and the Kohn–Sham density matrix. Methods using this result could significantly accelerate Kohn–Sham density functional theory calculations, as only a subset of the Kohn–Sham equations would need to be addressed. The result can also be seen as an explicit justification for the utility of frontier molecular orbital theory.

Keywords: Density functional theory – Linear scaling – Christoffel–Darboux formula – Frontier molecular orbitals

1 Motivation

Owing to its favorable cost per unit accuracy, density functional theory (DFT) is increasingly recognized as the method of choice for quantum chemistry calculations on large molecular systems [1, 2, 3, 4]. Most of the current research in DFT concentrates on improving these computational characteristics, either by increasing the accuracy of existing functionals (without incurring large computational penalties) or by decreasing the computational costs of extant DFT (without sacrificing accuracy).

This paper will explore an alternative method for accelerating Kohn–Sham calculations and so "linear scaling" methods, which are the typical approach to decreasing the computational costs of DFT calculations, bear mention [5, 6, 7, 8, 9, 10, 11, 12].

The defining feature of linear-scaling techniques is that the computational cost of such calculations grows only linearly with system size. (Especially in ordered solids, however, one often exceeds this standard by a logarithmic factor.) To achieve linear scaling, one must avoid solving the Kohn–Sham system of equations [13],

$$\left\{ \left(-\frac{\nabla}{2} + v_\sigma^{\mathrm{KS}}[\rho; r] \right) \psi_{i\sigma}(r) \equiv \varepsilon_{i\sigma} \psi_{i\sigma}(r) \right\}_{i=1}^{N_\sigma}; \ \sigma = \alpha, \beta \ , \tag{1}$$

where, in the usual notation, $\{\psi_{i\sigma}(r)\}_{i=1}^{N_\sigma}$ is the set of Kohn–Sham σ-spin orbitals, $\{\varepsilon_{i\sigma}\}_{i=1}^{N_\sigma}$ are their associated eigenvalues, the electron density is defined by

$$\rho(r) \equiv \rho_\alpha(r) + \rho_\beta(r)$$
$$\equiv \sum_{i=1}^{N_\alpha} |\psi_{i\alpha}(r)|^2 + \sum_{i=1}^{N_\beta} |\psi_{i\beta}(r)|^2 \ , \tag{2}$$

and

$$v_\sigma^{\mathrm{KS}}[\rho; r] \equiv v(r) + v_J[\rho; r] + v_{\mathrm{xc},\sigma}[\rho_\alpha, \rho_\beta; r] \tag{3}$$

is the Kohn–Sham potential. In Eq. (3), $v(r)$ is the external potential of the system of interest, $v_J[\rho; r] \equiv \int \frac{\rho(r)}{|r-r'|} \mathrm{d}r'$ is the Coulomb potential, and $v_{\mathrm{xc},\sigma}[\rho_\alpha, \rho_\beta; r] \equiv \frac{\delta E_{\mathrm{xc}}[\rho_\alpha, \rho_\beta]}{\delta \rho_\sigma(r)}$ is the σ-spin exchange–correlation potential. In a straightforward implementation, solving the Kohn–Sham equations involves diagonalizing large matrices, incurring a computational cost of $\mathrm{O}(m^3)$, where m is the number of one-electron basis functions or, in a fully numerical approach [14], the number of grid points. Linear-scaling techniques reduce this cost either by introducing cutoffs, either in the matrix elements of the Hamiltonian operator (divide-and-conquer technique) [7, 12] or in the elements of the first-order density matrix [5, 8]. In both techniques, the Kohn–Sham orbitals are never explicitly constructed.

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The method explored in this paper represents a new approach to the "density matrix family" of techniques, wherein the key problem becomes minimizing the Kohn–Sham energy as a functional of the density matrix,

$$E[\gamma_{KS}] \equiv \mathrm{Tr}\left[h^{KS}\gamma^{KS}\right] \ , \tag{4}$$

where

$$\gamma^{KS}(r,r') \equiv \gamma_{\alpha\alpha}^{KS}(r,r') + \gamma_{\beta\beta}^{KS}(r,r')$$
$$\equiv \sum_{i=1}^{N_\alpha} \psi_{i\alpha}^*(r')|\alpha\rangle\langle\alpha|\psi_{i\alpha}(r) + \sum_{i=1}^{N_\beta} \psi_{i\beta}^*(r')|\beta\rangle\langle\beta|\psi_{i\beta}(r) \tag{5}$$

and

$$\hat{h}^{KS} \equiv -\frac{\nabla_i^2}{2} + |\alpha\rangle v_\alpha^{KS}(r_i)\langle\alpha| + |\beta\rangle v_\beta^{KS}(r_i)\langle\beta| \ . \tag{6}$$

The difficulty arises because the minimization of the Kohn–Sham energy is subject to some constraints, most crucially those on the number of electrons

$$N_\alpha \equiv \int \gamma_{\alpha\alpha}^{KS}(r,r)\mathrm{d}r,$$
$$N_\beta \equiv \int \gamma_{\beta\beta}^{KS}(r,r)\mathrm{d}r \tag{7}$$

and the idempotency constraints

$$\gamma_{\alpha\alpha}^{KS}(r,r') \equiv \int \gamma_{\alpha\alpha}^{KS}(r,x)\gamma_{\alpha\alpha}^{KS}(x,r')\mathrm{d}x,$$
$$\gamma_{\beta\beta}^{KS}(r,r') \equiv \int \gamma_{\beta\beta}^{KS}(r,x)\gamma_{\beta\beta}^{KS}(x,r')\mathrm{d}x \ . \tag{8}$$

The idempotency constraint is particularly problematic, and it is often enforced using some sort of "penalty function." It is more efficient, however, to write the density matrices as a product of a symmetric matrix and its generalized inverse [5]

$$\gamma_{\sigma\sigma}^{KS}(r,r') \equiv \int \beta_{\sigma\sigma}^-(r,x)\beta_{\sigma\sigma}(x,r')\mathrm{d}x \tag{9}$$

and then minimize the analogue of Eq. (4),

$$E[\gamma_{KS}] \equiv \mathrm{Tr}\left[H^{KS}\beta^-\beta\right] \ , \tag{10}$$

with respect to $\beta(x, r)$, using a chemical potential to force the constraints of Eq. (7). From Eq. (10) many different computational approaches can be constructed, including the nonorthogonal localized orbital methods proposed by Yang [5].

Note that in the previous procedure, we never used the fact that the Kohn–Sham orbitals are orthonormal eigenvectors of a common effective potential. One anticipates, then, that employing this highly specific

information about the relationship between the Kohn–Sham orbitals to construct the Kohn–Sham density matrix would allow one to obtain a new procedure with greater computational efficiency. This is the primary motivation for the present work.

The justification for seeking an improved linear-scaling technique is if the method so developed has the potential to supercede many of the problems with existing techniques. The most important problem with existing linear-scaling techniques is their extreme inefficiency for small systems. This is easily understood for a technique like that sketched earlier: for small systems, we have merely replaced a single $O(m^3)$ operation (diagonalization of the Kohn–Sham Hamiltonian matrix) with numerous other $O(m^3)$ operations—the matrix multiplications in Eq. (9) and the construction of the generalized inverse are performed repeatedly during the iterative minimization of Eq. (4). Consequently, linear-scaling techniques are typically more costly than the more simple "direct diagonalization" approach for systems less than 10 Å across.

Another drawback to typical linear-scaling Kohn–Sham DFT approaches is that the Kohn–Sham molecular orbitals are never constructed. The Kohn–Sham molecular orbitals, and especially the frontier molecular orbitals, contain chemically useful information about the reactivity of the molecule being studied, and it is desirable to study them when performing calculations, both for the chemical insight they provide and because an unreasonable set of Kohn–Sham orbitals and orbital eigenvalues is the most transparent indicator of a calculation that has gone awry. Unfortunately, in a typical linear-scaling Kohn–Sham DFT approach, these orbitals are rarely accessed until after the calculation is completed, and then finding the highest occupied orbitals and lowest unoccupied orbitals requires partial diagonalization of the Kohn–Sham Hamiltonian (or density matrix). Among other drawbacks, this hinders one in identifying and stopping errant calculations early in the computational process.

An ideal Kohn–Sham DFT technique, then, would be competitive with simple diagonalization for small systems, competitive with linear-scaling techniques for large systems, and would provide access to approximate frontier molecular orbitals throughout the course of the calculation. The present paper represents a first attempt to explore methods that might meet these criteria.

2 Theoretical background

The genesis of this study is the Christoffel–Darboux formula for orthogonal polynomials [15],

$$\sum_{i=0}^n \rho_i(x)\rho_i(x') \equiv a_n \frac{\rho_n(x')\rho_{n+1}(x) - \rho_n(x)\rho_{n+1}(x')}{(x - x')} \ , \tag{11}$$

where, because the $\{\rho_n(x)\}_{n=0}^\infty$ are a set of polynomials orthonormal to a nonnegative weight function,

$$\int \rho_i(x)\rho_j(x)\omega(x)\mathrm{d}x \equiv \delta_{ij} \ , \tag{12}$$

they satisfy a three-term recursion relation:

$$a_n \rho_{n+1}(x) = (x - b_n)\rho_n(x) - a_{n-1}\rho_{n-1}(x). \tag{13}$$

Favard's theorem dictates that $a_n > 0$ for all n [15].

That the Christoffel–Darboux formula might be useful for quantum chemistry was first recognized by Dawson and March [16]: note that if the orthogonal polynomials were Kohn–Sham spin orbitals, then Eq. (11) expresses the Kohn–Sham density matrix for this spin in terms of the highest occupied and the lowest unoccupied Kohn–Sham orbitals. Two major obstacles remain. The first is that, excepting the case of spherical symmetry, we are rarely concerned with Kohn–Sham orbitals that depend upon only one spatial variable. The second obstacle is that, even in one dimension, the eigenfunctions of the one-dimensional Schrödinger equation,

$$\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + v^{\mathrm{KS}}(x) \right)\psi_i(x) = \varepsilon_i \psi_i(x) \ , \tag{14}$$

only satisfy a three-term recurrence relation (Eq. 13) for very special choices of the Kohn–Sham potential, $v^{\mathrm{KS}}(x)$.

Exploiting the Christoffel–Darboux formula in Kohn–Sham DFT, then, requires generalizing the three-term recurrence relation to three dimensions in such a way that

1. The three-dimensional three-term recurrence relation will yield a generalized Christoffel–Darboux formula.
2. Kohn–Sham potentials have orbitals satisfying this generalized recurrence relation.

These obstacles are surmounted in Sects. 3 and 4, respectively. To motivate these results, however, we prove that the frontier Kohn–Sham molecular orbitals provide sufficient information to determine not only the Kohn–Sham density matrix, but every property of an electronic system.

Theorem 1. Suppose the highest occupied orbitals of each spin are known for the system. In addition, the lowest unoccupied orbitals, including any orbitals with lower orbital energies than the highest occupied orbitals, are known for each spin channel. Together, these orbitals determine every property of the system.

Proof: Take one orbital of each spin. We can determine the Kohn–Sham potential for these systems by inverting the Kohn–Sham equations,

$$v_\alpha^{\mathrm{KS}}(r) \equiv \frac{\left(\frac{\nabla^2}{2} + \varepsilon_{j,\alpha}\right)\psi_{j,\alpha}(r)}{\psi_{j,\alpha}(r)} \cdot$$

$$v_\beta^{\mathrm{KS}}(r) \equiv \frac{\left(\frac{\nabla^2}{2} + \varepsilon_{j,\beta}\right)\psi_{j,\beta}(r)}{\psi_{j,\beta}(r)} \ , \tag{15}$$

(Where Eq. (15) gives an indeterminate form (as the nodal surfaces of orbitals), the potential may be evaluated using L'Hôpital's rule.) Solving the Kohn–Sham equations for these potentials, we can construct the electron density,

$$\rho(r) \equiv \sum_{i=1}^{\infty} \eta_{i\alpha}|\psi_{i\alpha}(r)|^2 + \sum_{i=1}^{\infty} \eta_{i\beta}|\psi_{i\beta}(r)|^2 \ , \tag{16}$$

if we know which orbitals are occupied and which orbitals are unoccupied. Knowing the highest occupied orbitals allows us to determine the upper limit of the summation in Eq. (16). When there are no holes below the Fermi level – that is, when the system is Kohn–Sham v-representable – the information from the lowest unoccupied orbitals is redundant. When there are holes below the Fermi level, knowing the lower unoccupied orbitals tells us which orbitals they are [17].

It must be noted that this theorem has been circulating orally, if not in print, for many years. It also should be noted that it is not true (though it is often stated) that a single Kohn–Sham orbital determines all the properties of a system. In the spin-free case, even knowing the highest occupied orbital is not enough. To see this, consider that the highest occupied molecular orbital for the helium atom is $\sqrt{\rho_{\mathrm{He}}(r)}$. However, knowing that this is the highest occupied molecular orbital does not distinguish between the helium atom and another pure-state v-representable system, namely the one-electron system with electron density $\frac{1}{2}\rho_{\mathrm{He}}(r)$. Consistent with the spin-restricted analogue of the previous theorem, however, the lowest unoccupied Kohn–Sham orbitals for these two systems differ. In the spin-unrestricted case, there are two highest occupied molecular orbitals for the helium atom but only one for the system with electron density $\frac{1}{2}\rho_{\mathrm{He}}(r)$.

Theorem 1 indicates that, in principle, knowledge of the frontier molecular orbitals is sufficient to determine the density matrix. However, the construction in the proof of theorem 1 constructs the density matrix from the Kohn–Sham orbitals by returning to the original Kohn–Sham problem (which could be solved either by straight diagonalization or with linear-scaling techniques). Progress, then, depends on forming the Kohn–Sham density matrix as an explicit functional of the frontier Kohn–Sham orbitals.

3 The matrix-vector three-term recurrence relation

We restrict ourselves to the Kohn–Sham equation for α-spin electrons, the case for β-spin electrons being identical. The following discussion is limited to three dimensions, but the extension to other dimensions is straightforward. In three dimensions, we can write any analytic function as a power series in

$$f(r) = \sum_{|k|=0}^{\infty} a_k r^k , \qquad (17)$$

where $k^T \equiv [k_1, k_2, k_3]$, $r^k = r_1^{k_1} r_2^{k_2} r_3^{k_3}$, $|k| = k_1 + k_2 + k_3$, and k_1, k_2, and k_3 are nonzero integers. Nonanalytic functions may be approximated arbitrarily closely using functions of the form of Eq. (17); moreover, the extension of these results to multidimensional Laurent series [18] is also straightforward. A three-dimensional polynomial is said to have degree d if it can be written in the general form

$$P_d(r) \equiv \sum_{|k|=0}^{d} a_k r^k. \qquad (18)$$

Problems arise when one seeks to extend classical results like the Christoffel–Darboux formula to higher dimensions because, for $d > 0$, there are generally many different ways to choose k_1, k_2, and k_3 so that $|k| = k_1 + k_2 + k_3$. To state this more mathematically: the number of linearly independent three-dimensional polynomials with degree d is

$$r_d^3 = \binom{d+2}{d} , \qquad (19)$$

which differs form the one-dimensional result $(r_d^1 = 1)$. However, many analogues to one-dimensional results can be obtained if, instead of treating individual orthogonal polynomials, one treats vectors of orthogonal polynomials with a given degree [19, 20, 21, 22, 23]. That is, for each degree, d, define r_d^3-dimensional vector functions that are orthonormal with respect to the weight function $\omega(r)$,

$$P_d^T \equiv \left[P_d^1(r), P_d^2(r), \ldots P_d^{r_d^3}(r) \right]. \qquad (20)$$

The orthonormality constraint may be compactly expressed as

$$\int P_d^T(r) \times P_d(r) \omega(r) \mathrm{d}r = I, \qquad (21)$$

where $\times$ denotes the outer product,

$$P_d^T(r) \times P_d(r) \equiv$$

$$\begin{bmatrix} P_d^1(r)P_d^1(r) & P_d^2(r)P_d^2(r) & \cdots & P_d^1(r)P_d^{r_d^3}(r) \\ P_d^2(r)P_d^1(r) & P_d^2(r)P_d^2(r) & & p_d^2(r)P_d^{r_d^3}(r) \\ \vdots & \vdots & \ddots & \vdots \\ P_d^{r_d^3}(r)P_d^1(r) & P_d^2(r)P_d^{r_d^3}(r) & \cdots & P_d^{r_d^3}(r)P_d^{r_d^3}(r) \end{bmatrix},$$

$$(22)$$

and I is the $r_d^3 \times r_d^3$ identity matrix. Polynomials with different degrees are orthogonal in an set of orthogonal polynomials, so

$$\int P_{d'}^T(r) \times P_d(r) \omega(r) \mathrm{d}r = \mathbf{0} \quad d \neq d', \qquad (23)$$

where $\mathbf{0}$ is a $r_{d'}^3 \times r_d^3$ matrix of zeros [20].

To derive the Christoffel–Darboux formula requires an analogue to the recursion relation for one-dimensional orthogonal polynomials. A natural extension is [20]

$$r_i P_n(r) = A_n^i P_{n+1}(r) + B_n^i P_n(r) + \left(A_{n-1}^i\right)^T P_{n-1}(r), \qquad (24)$$

with $P_{-1}(r) = A_{-1}^i = 0$.

From the dimension of the vectors, $\{P_n(r)\}_{n=0}^{\infty}$ we discern that A_n^i is a $r_n^3 \times r_{n+1}^3$ matrix and B_n^i is a $r_n^3 \times r_n^3$ matrix. We call Eq. (24) the matrix-vector recurrence relation.

The matrix-vector recurrence relation is a fundamental mathematical result, motivated by the fact that for any set of polynomials generated by the form (Eq. 24) (subject to a rank condition on the matrices $\{A_d^i\}_{i+1}^3$ and the choice $P_0(r) = 1$, there will always exist some $\omega(r)$ for which Eqs. (21) and (23) are satisfied. In the one-dimensional case, the preceding result becomes Favard's theorem, and the three-term recursion relation assumes its classical form [19, 20].

With this background we can derive an analogue to the Christoffel–Darboux theorem, namely [20]

$$\sum_{i=0}^{n} P_i(r) \cdot P_i(r') = \sum_{i=0}^{n} \sum_{j=1}^{r_n^3} P_i^j(r) P_i^j(r')$$

$$= \frac{P_n(r') \cdot A_n^i P_{n+1}(r) - P_n(r) \cdot A_n^i P_{n+1}(r')}{r_i - r_i'} \qquad (25)$$

Equation (25) and, more generally, the matrix-vector ansatz for multidimensional orthogonal polymials, was first derived by Xu [20].

Proof of Eq. (25): We proceed by induction. For $n = 0$, we have

$$\frac{P_0(r') \cdot A_0^i P_1(r) - P_0(r) \cdot A_0^i P_1(r')}{r_i - r_i'}$$

$$= \frac{P_0(r')\left[r_i P_0(r) - B_0^i P_0(r)\right] - P_0(r)\left[r_i' P_0(r') - B_0^i P_0(r')\right]}{r_i - r_i'}$$

$$= \frac{(r_i - r_i')P_0(r')P_0(r)}{r_i - r_i'} + \frac{P_0(r') \cdot B_0^i P_0(r) - P_0(r)B_0^i P_0(r')}{r_i - r_i'}$$

$$= P_0(r')P_0(r)$$

$$(26)$$

Now, suppose the Christoffel–Darboux formula holds for some n. Then

$$\sum_{i=0}^{n+1} P_i(r) \cdot P_i(r')$$

$$= \frac{P_{n+1}(r') \cdot A_{n+1}^i P_{n+2}(r) - P_{n+1}(r) \cdot A_{n+1}^i P_{n+2}(r')}{r_i - r_i'}$$

$$= \frac{\begin{pmatrix} P_{n+1}(r') \cdot \left[r_i P_{n+1}(r) - B_{n+1}^i P_{n+1}(r) - \left(A_n^i\right)^{\mathrm{T}} P_n(r) \right] \\ -P_{n+1}(r) \cdot \left[r_i' P_{n+1}(r') - B_{n+1}^i P_{n+1}(r') - \left(A_n^i\right)^{\mathrm{T}} P_n(r') \right] \end{pmatrix}}{r_i - r_i'}$$

$$= \frac{1}{r_i - r_i'} \begin{pmatrix} (r_i - r_i') P_{n+1}(r) P_{n+1}(r') \\ -P_{n+1}(r') B_{n+1}^i P_{n+1}(r) + P_{n+1}(r) B_{n+1}^i P_{n+1}(r') \\ -P_{n+1}(r') \left(A_n^i\right)^{\mathrm{T}} P_n(r) + P_{n+1}(r) \left(A_n^i\right)^{\mathrm{T}} P_n(r') \end{pmatrix}$$

$$= P_{n+1}(r) P_{n+1}(r') + \frac{P_n(r') A_n^i P_{n+1}(r) - P_n(r) A_n^i P_{n+1}(r')}{r_i - r_i'}$$

$$+ P_{n+1}(r) B_{n+1}^i P_{n+1}(r') - P_{n+1}(r') B_{n+1}^i P_{n+1}(r)$$

$$= P_{n+1}(r) P_{n+1}(r') + \sum_{i=0}^{n} P_i(r) \cdot P_i(r'). \tag{27}$$

The potential importance of the generalized Christoffel–Darboux formula is clear: if one can find an efficient way to construct the function $P_n(r') \cdot A_n^i P_{n+1}(r)$, then we can also construct the density matrix. Moreover, constructing $P_n(r') \cdot A_n^i P_{n+1}(r)$ requires knowledge only of the highest occupied and lowest unoccupied states, along with the fundamental multidimensional recursion relation. For orthogonal polynomials, the recurrence matrices are simply computed from $P_n(r)$ and $P_{n+1}(r)$, see Eq. (30).

One problem remains: the Kohn–Sham orbitals for physical systems will rarely, if ever, be orthogonal polynomials. As such, practical applications of the Christoffel–Darboux formula require generalizing the matrix-vector recurrence relation, Eq. (24), to include the Kohn–Sham orbitals of relevant physical systems. This is the topic of the next section.

4 Generalizing the recurrence relation

Motivated by the derivation (Eq. 27), we generalize the matrix-vector recurrence relation to

$$\hat{x}_i(r) = A_n^i F_{n+1}(r) + B_n^i F_n(r) + \left(A_{n-1}^i\right)^{\mathrm{T}} F_{n-1}(r), \tag{28}$$

where $F_{-1}(r) = A_{-1}^i = 0$, $F_0(r)$ and B_0^i are arbitrary, and $\{\hat{x}_i(r)\}_{i=1}^3$ are operators that satisfy the following constraints:

1. The operator $\hat{x}_i(r) - \hat{x}_i(r')$ has a left-inverse unless $r \neq r'$.
2. $\hat{x}_i(r)[kf(r)] = k\hat{x}_i(r)f(r)$, where k is a constant. While $\hat{x}_i$ need not be a linear operator, theorem 2 will show that it can be assumed to be.

3. Since the $\{\hat{x}_i(r)\}_{i=1}^3$ operators need not commute amongst themselves, we allow the number of rows and columns in A_n^i and B_n^i to vary as long as their dimensions remain consistent with the requirements of Eq. (28). That is, while A_n^i is still an $r_n^3 \times r_{n+1}^3$ matrix and B_n^i is still an $r_n^3 \times r_n^3$ matrix, r_n^3 need not be given by Eq. (19). (The dimensions of the matrices are not totally arbitrary however: the form of the recursion implies that $r_n^3 \leq 3^n$.)

We refer to the $\{\hat{x}_i(r)\}_{i=1}^3$ as recursion operators.

Retracing the proof of Eq. (25) with this new relation reveals that the Christoffel–Darboux formula now holds in the revised form:

$$\sum_{i=0}^{n} F_i(r) \cdot F_i(r') = \sum_{i=0}^{n} \sum_{j=1}^{r_n^3} F_i^j(r) F_i^j(r') =$$
$$[\hat{x}_i(r) - \hat{x}_i(r')]^{-1} \left[F_n(r') \cdot A_n^i F_{n+1}(r) - F_n(r) \cdot A_n^i F_{n+1}(r') \right]. \tag{29}$$

Enumerating and rationalizing the generalizations in Eq. (28) may be helpful.

1. The functions $F_n(r) \equiv \left[F_n^1(r), F_n^2(r), \ldots F_n^{r_n^3}(r) \right]^{\mathrm{T}}$ do not have to be polynomials and $F_0(r)$ is arbitrary. This choice significantly expands the robustness of the recursion. For instance, because the three-dimensional harmonic oscillator eigenfunctions can be written in the form $F_n(r) = \sigma(r) P_n(r)$, where the components of $P_n(r)$ are products of the classical Hermite polynomials and $\sigma(r)$ is the appropriate Gaussian function, the three-dimensional harmonic oscillator is now within the purview of the Christoffel–Darboux equation.

2. The recursion operators, $\{\hat{x}_i(r)\}_{i=1}^3$, need not denote multiplication by the Cartesian coordinates (x, y, z) and are, in general, operators. The simplest case is when the recursion operators simply multiply the operand by a function of the Cartesian coordinates, $\{x_i(r)\}_{i=1}^3$. With this extension, the Christoffel–Darboux formula encompasses Kohn–Sham equations that can be changed into differential equations with orthogonal polynomial eigenvectors by a coordinate transformation. (The invertibility restriction ensures that the coordinate transformation from r to $\{x_i(r)\}_{i=1}^3$ is invertible.)

3. Relaxing the dimensional requirement from Eq. (19) is essential if the operators $\{\hat{x}_i(r)\}_{i=1}^3$ do not commute, since then the number of linearly independent functions of a given "degree" in these operators will exceed the prediction of Eq. (19). In addition, in systems with high symmetry the "natural ordering" of states sometimes seems to favor a higher level of "pseudodegeneracy" than that predicted by Eq. (19). (For example, Eq. 19 is inconsistent with grouping the orbitals of atomic systems by their principle quantum numbers.)

Allowing the $\{\hat{x}_i(r)\}_{i=1}^3$ to be operators significantly extends the purview of the recurrence relation. Some insight is gained by exploring the links between the recursion operators and the recursion matrices. First, multiplying Eq. (28) by $F_{n+1}^T(r)$ and integrating we obtain

$$A_n^i = \int F_{n+1}^T(r) \times \hat{x}_i(r)F_n(r)\,dr, \tag{30}$$

where we have used analogues of Eqs. (21) and (23). Similar multiplication by $F_n^T(r)$ gives

$$B_n^i = \int F_n^T(r) \times \hat{x}_i(r)F_n(r)\,dr. \tag{31}$$

These results might have been deduced directly from similar expressions for the recursion coefficients of orthogonal polynomials [20, 24].

Equation (30) is an especially important result. If we know $F_n(r)$, $F_{n+1}(r)$, and one of the recursion operators, $\hat{x}_i(r)$, then we can use Eq. (30) to evaluate the A_n^i, and thereby evaluate the Christoffel–Darboux equation (Eq. 29). Equation (30) also indicates that it is reasonable to assume that the matrices A_n^i usually achieve the maximum possible rank of r_n^3. From Eq. (30), this implies that for every r_n^3-component vector c,

$$\int F_{n+1}^j(r) \sum_{i=1}^{r_n^3} c_i\hat{x}_i(r)F_n^i(r)\,dr \neq 0 \tag{32}$$

for at least one value of j. Equation (32) could only be violated if the elements of $F_{n+1}(r)$ do not form a complete basis set for the space of all functions in which the $\{\hat{x}_i\}_{i=1}^3$ are applied, in some combination, at least $n+1$ times but no more. [That is, the "degree" of $F_{n+1}(r)$ is $n+1$. If this assumption is not true, one can envision using the flexibility provided in generalization 3 to increase r_{n+1}^3 until full rank is attained.] Given that the rank A_n^i is r_n^3, one can obtain a generalized inverse, an $r_{n+1}^3 \times r_n^3$ matrix $(A_n^i)^-$ satisfying

$$\sum_{i=1}^3 (A_n^i)^- A_n^i = I. \tag{33}$$

Using this inverse, we may rewrite the recursion relation in the form [20]

$$F_{n+1}(r) = \sum_{i=1}^3 (A_n^i)^- \hat{x}_i(r)F_n(r) - C_n^i F_n(r) - D_n^i F_{n-1}(r). \tag{34}$$

It is also helpful to note that the $\hat{x}_i(r)$ are a sort of ladder operator [25]. This follows directly from the "contamination relation",

$$A_n^i F_{n+1}(r) + B_n^i F_n(r) + (A_{n-1}^i)^T F_{n-1}(r) \equiv \hat{x}_i(r)F_n(r), \tag{35}$$

which shows that the effect of operation by $\hat{x}_i(r)$ is to "contaminate" states of degree n with their "raised" (degree $n+1$) and "lowered" (degree $n-1$) counterparts. It is particularly instructive that when the $\{\hat{x}_i\}_{i=1}^3$ are linear, mutually commuting, operators, the eigenfunctions all have the form

$$F_n^l(r) = \sum_{|k|=0}^n a_k^l \cdot \hat{x}_1^{k_1}(r)\hat{x}_2^{k_2}(r)\hat{x}_3^{k_3}(r). \tag{36}$$

The $\{\hat{x}_i\}_{i=1}^3$ generalize the form of the conventional "raising" ladder operator, where $a_k^l = 0$ for all $|k| < d$.

It is useful to establish a link between the recursion operators and the Hamiltonian. For simplicity, we start with the one-dimensional case. Applying the Kohn–Sham Hamiltonian, $\hat{h}(x)$, to both sides of the generalized form of Eq. (13),

$$a_n\psi_{n+1}(x) = [\hat{q}(x) - b_n]\psi_n(x) - a_{n-1}\psi_{n-1}(x) \tag{37}$$

and using the eigenvalue condition

$$\hat{h}\psi_n(x) = \varepsilon_n\psi_n(x) \tag{38}$$

we obtain

$$a_n\varepsilon_{n+1}\psi_{n+1}(x) = \left(\hat{h}\hat{q} - b_n\varepsilon_n\right)\psi_n(x) - a_{n-1}\varepsilon_{n-1}\psi_{n-1}(x). \tag{39}$$

Subtracting ε_{n+1} times Eq. (37) yields the identity

$$\left(\hat{h} - \varepsilon_{n+1}\right)\hat{q}(x)\psi_n(x) = (\varepsilon_n - \varepsilon_{n+1})b_n\psi_n(x)$$
$$+ a_{n-1}(\varepsilon_{n-1} - \varepsilon_{n+1})\psi_{n-1}(x). \tag{40}$$

Equation (40) is a sort of "lowering" contamination relation: when $\hat{h}\hat{q}$ operates on an eigenfunction of $\hat{h}$, $\psi_n(x)$, it tends to mix $\psi_n(x)$ with the eigenfunction of next-lowest order.

Similar relations are obtained in higher dimensions. Applying the Kohn–Sham Hamiltonian operator to each side of Eq. (28) gives

$$\hat{h}\hat{x}_i(r)F_n(r) = A_n^i E_{n+1}F_{n+1}(r) + B_n^i E_n F_n(r)$$
$$+ (A_{n-1}^i)^T E_{n-1}F_{n-1}(r), \tag{41}$$

where E_n is the $r_n^3 \times r_n^3$ diagonal matrix whose diagonal elements are the Kohn–Sham energy eigenvalues, $\hat{h}F_{n-1}^i(r) = (E_n)_{ii}F_{n-1}^i(r)$ and A_n^i and B_n^i depend on the recursion operators through Eqs. (30) and (31). A sim-

pler form, more closely analogous to Eq. (40), is obtained if we apply $\hat{h}$ to both sides of Eq. (34). Then

$$
E_{n+1}F_{n+1}(r) = \sum_{i+1}^{3} \left(A_n^i\right)^{-}\hat{h}(r)\hat{x}_i(r)F_n(r) - C_n^i E_n F_n(r)
$$
$$
- D_n^i E_{n-1}F_{n-1}(r). \tag{42}
$$

Multiplying both sides of Eq. (34) by E_{n+1} and subtracting from Eq. (42) gives a result analogous to Eq. (40), namely

$$
\sum_{i=1}^{3} \left[\left(A_n^i\right)^{-}\hat{h}(r) - E_{n+1}\left(A_n^i\right)^{-}\right]\hat{x}_i(r)F_n(r)
$$
$$
= \left(C_n^i E_n - E_{n+1}C_n^i\right)F_n(r) \tag{43}
$$
$$
+ \left(D_n^i E_{n-1} - E_{n+1}D_n^i\right)F_{n-1}(r).
$$

Equations (40), (41) and (43) are equations for the recursion operators, $\{\hat{x}_i\}_{i=1}^{3}$, and solving these equations for each n will give an appropriate solution. Matters are complicated because solving Eq. (41) or (43) for one specific value of n may not give the general solution. For example, one solution to Eq. (40) is

$$
\hat{q}(x) \equiv b_n + a_{n-1}\hat{l}(x) \tag{44}
$$

where $\hat{l}(x)$ is the "lowering" ladder operator,

$$
\hat{l}(x)\psi_k(x) = \psi_{k-1}(x). \tag{45}
$$

This is the "trivial solution" – substitution of Eq. (44) into Eq. (37) gives $a_n = 0$.

5 Universality of the generalized recursion relation

It was demonstrated in Sect. 3 that the three-term recursion relation has a natural generalization to higher dimensions, namely, the matrix-vector recursion relation, Eq. (24). It was then shown in Sect. 4 how this relation could be dramatically extended, Eq. (28), while still maintaining the sought Christoffel–Darboux relation, Eq. (29). Does every set of Kohn–Sham orbitals satisfy a recursion relation with the form of Eq. (28)?

Theorem 2: Let $\{F_n(r)\}_{n=0}^{\infty}$ be a set of orthonormal functions, with $\dim\left(F_n \equiv r_n^3\right)$. There exist linear operators, $\{\hat{x}_i(r)\}_{i=1}^{3}$, such that $\{F_n(r)\}_{n=0}^{\infty}$ satisfy a matrix-vector recursion with the form of Eq. (28).

The proof is trivial. It is sufficient to show that, for any choice of the recursion matrices, there exist operators $\{\hat{x}_i(r)\}_{i=1}^{3}$ that satisfy the matrix-vector recursion relation. Adopting the standard bra-ket notation, it is evident from Eq. (28) that

$$
\hat{x}_i(r) = \sum_{n=0}^{\infty} \left|A_n^i F_{n+1}(r) + B_n^i F_n(r) + \left(A_{n-1}^i\right)^{\mathrm{T}}F_{n-1}(r)\right\rangle\langle F_n(r)|. \tag{46}
$$

The component-by-component resolution of this relationship is instructive:

$$
\hat{x}_i(r)F_n^k(r) = \sum_{l=1}^{r_{n+1}^3} \left(A_n^i\right)_{kl}F_{n+1}^l(r) + \sum_{l=1}^{r_n^3} \left(B_n^i\right)_{kl}F_n^l(r)
$$
$$
+ \sum_{l=1}^{r_{n-1}^3} \left(A_{n-1}^i\right)_{kl}F_{n-1}^l(r), \tag{47}
$$

where $F_n^l(r)$ denotes the lth component of $F_n(r)$ and $(D)_{kl}$ denotes the element in the kth row and lth column of matrix $\mathbf{D}$.

Theorem 2 is only a formal result, and similar results are available for any reasonable recurrence relation. The hope is that because the $\{F_n(r)\}_{n=0}^{\infty}$ are very special functions – eigenfunctions of a second-order differential operator grouped together in an obvious way – the recursion operators can be accurately approximated with a simple form. While the motivation for the generalized matrix-vector recursion relation is the preservation of the Christoffel–Darboux relation, clearly the recursion relation is conducive to a simple analytic form. For example, the form of the recursion operators in Eq. (28) takes a very simple form when the eigenfunctions are related to orthogonal polynomials – as by coordinate transformation and multiplication by a weighting function – are much simpler for than other recursions, for example, the ladder operators [26, 27]. Generally speaking, the action of a second-order differential operator is to "reduce the degree" of a function by two orders, so the fact the elements of $\{F_n(r)\}_{n=0}^{\infty}$ satisfy a linear second-order partial differential equation is also favorable.

From Eq. (46) for the recursion operators and Eqs. (30) and (31) for the recurrence matrices, it is apparent that there are generally many different recursion operators that satisfy Eq. (46), and each choice of recursion operators gives different recurrence matrices through Eqs. (30) and (31). Conversely, for any given set of orthogonal polynomials one can choose many different recurrence matrices, the recursion operators subsequently being defined by Eq. (46). Since it is straightforward to determine the recurrence matrices from the recursion operators, we should exploit this freedom and choose recursion operators with simple forms. In the remainder of the paper we shall assume that recursion operators, $\{\hat{x}_i(r)\}_{i=1}^{3}$, are chosen so that they are as simple and "easily approximated" as possible, with the form of the recurrence matrices, $\{A_n^i\}_{i=1}^{3}$ and $\{B_n^i\}_{i=1}^{3}$, being subsequently determined by this form through Eqs. (30) and (31).

6 Proposed computational procedure

For completeness, we sketch how solutions to the Kohn–Sham equations, or any other independent particle model with a local effective potential, could be obtained from the preceding analysis.

1. Starting from an initial "guessed" electron density, $\rho_0^{\alpha,\beta}(r)$, construct the Kohn–Sham Hamiltonian, Eq. (6).
2. From this Hamiltonian, find at least one of the recursion operators, $\hat{x}_i(r)$.
3. Solve for the α-spin eigenvalues, $F_{n_\alpha-1}^\alpha(r)$ and $F_{n_\alpha}^\alpha(r)$, where n_α is the smallest numbers such that

$$\int \left[\sum_{i=0}^{n_\alpha} F_i^\alpha(r) \cdot F_i^\alpha(r) \right] \mathrm{d}r > N_\alpha. \tag{48}$$

In practice, it may be necessary to solve instead for $F_{n_\alpha}^\alpha(r)$ and $F_{n_\alpha+1}^\alpha(r)$, since the energetic order of eigenfunctions may differ from the order in which they are generated by the recursion relation. Use Eq. (30), find the recurrence matrix, A_n^i. Owing to the form of Eq. (30), the recursion matrices are expected to be sparse. In the extreme case of a separable partial differential equation, the recursion matrices, A_n^i, have exactly one nonzero element in each row.

Equation (48) can be evaluated using the Christoffel–Darboux formula. The technique for the β-spin electrons is identical.

4. Using the criterion of lowest energy, construct the density matrix by "subtracting off" the unoccupied orbitals from the Christoffel–Darboux result. That is, evaluate the α-spin density matrix (Eq. 49) and its β-spin counterpart, and then construct the Kohn–Sham density matrix from Eq. (5).

$$\gamma_{\alpha\alpha}^{\mathrm{KS}}(r) \equiv \sum_{i=0}^{n_\alpha} F_i^\alpha(r) \cdot F_i^\alpha(r') - \sum_{\mathrm{unoccupied}} F_m^{j;\alpha}(r) F_m^{j;\alpha}(r') \tag{49}$$

5. From the trace of the density matrix components, construct the spin densities, guess a new Kohn–Sham Hamiltonian, and repeat steps 2–5 until convergence.

This algorithm would be immediately practicable were it not for step 2. If we assume that step 2 can be performed in an efficient fashion, all we must do is solve for a select few of the Kohn–Sham eigenfunctions or, in the spirit of linear scaling methods, perhaps work to construct "directly" the numerator on the right-hand side of the Christoffel–Darboux relation. In either case, the algorithm would be competitive with existing techniques.

Whether there is an efficient, accurate, and robust way to construct approximations to the recursion operators is a topic for further research. Several tools at our disposal were presented in Sect. 4, perhaps the most helpful of these are Eqs. (41) and (43), which link the recursion operators to the structure of the Kohn–Sham Hamiltonian. The matrix-vector form of the recurrence relation chosen here is designed to exploit some underlying properties of the Kohn–Sham problem: the fact that a second-order differential operator "reduces the degree" of a function by 2 orders motivates the choice of a two-level recursion relation, while the quasidegeneracy structure of differential equations in higher dimensions is captured in the "matrix-vector" form of the recursion relation. For this reason, this recursion has an especially simple form whenever the system can be mapped onto an "classical" differential equation, and this presents one way to proceed: attempt to find a transformation of coordinates – probably quite nonlinear – under which the partial differential equation of interest approximates a system whose recursion coefficients are known. Another possibility is to assume a form for the recursive operator, for example,

$$\begin{aligned} \hat{x}_i(r) \equiv & \, a_i^{(0)}(r) \cdot + a_i^{(1)}(r) \nabla b_i^{(1)}(r) \cdot \\ & + a_i^{(2)}(r) \nabla b_i^{(2)}(r) \nabla c_i^{(2)}(r) \cdot + \cdots, \end{aligned} \tag{50}$$

solve for the coefficients using the first few orders of Eq. (41) and hope the recursion operators are also valid at higher orders.

To find a truly robust approach, however, will require further study of the properties of the Kohn–Sham Hamiltonian. It is known that the Kohn–Sham Hamiltonian is a sort of "generalized" Sturm–Liouville operator, satisfying theorems analogous to those of classical Sturm–Liouville equations [28]. Indeed, Wintner's generalized nodal theorem [28] is one of the primary motivations for the vector-matrix recursion structure adopted here. The author hopes that by studying the properties of the Kohn–Sham differential operator, methods for approximately constructing the recursion operators directly from the Kohn–Sham potential will be obtained. If the methods for doing so are no more costly than steps 3 and 4 in the previous algorithm, one may anticipate an entirely new approach for solving the Kohn–Sham equations, as well as other partial differential equations with similar form.

In passing, we note that the similarities of the present proposal to pseudopotential techniques [29, 30, 31, 32, 33]. In both cases, only the "chemically relevant" valence orbitals are constructed. However, in the present proposal the effects of the "core" electrons are modeled exactly through the Christoffel–Darboux relation. It will be interesting to assess how closely the orbitals from pseudopotentials satisfy Eq. (29), and it is interesting to contemplate using the Christoffel–Darboux formula as a constraint by which improved pseudopotentials might be constructed.

Also in passing, we mention that the result of the Christoffel–Darboux formula is nothing less than the

"resolution of the identity" in the basis set of the occupied and lower unoccupied valence orbitals. Thus, the Christoffel–Darboux formula has immediate computational applications in "resolution of the identity" techniques for accelerating electronic structure calculations [34, 35, 36]. (For a basis set of orthogonal polynomials, the benefit is immediate. For the more common Gaussian basis sets, existing techniques may be more efficient.)

7 Conclusion

The key result of this paper is the generalized "matrix recurrence relation", Eq. (28) and the associated Christoffel–Darboux formula, Eq. (29). Theorem 2 shows that the present construction generalizes Dawson and March's results for the orbitals of the one-dimensional harmonic oscillator [16] to the orbitals of any system of noninteracting fermions. The Christoffel–Darboux formula is an explicit method for determining the reactivity of a chemical system from a few of the highest occupied and lowest unoccupied Kohn–Sham molecular orbitals, and thus provides a rigorous mathematical justification for frontier molecular orbital theory. In addition, after one performs a conventional Kohn–Sham DFT calculation, one may evaluate the recursive operators and recursion matrices using Eqs. (48) and (30), thereby obtaining an interesting identity relating the valence Kohn–Sham orbitals to the entire Kohn–Sham density matrix.

The primary goal of this line of research, however, is to derive efficient, accurate, and robust computational methods for generating the recursion operators from the Kohn–Sham potential. The favorable properties of the proposed recurrence relation – the freedom in choosing the recurrence matrices, the two-level nature of the recurrence, and the explicit accommodation of the nodal structure and quasidegeneracy of eigenfunctions – lead the author to hope that the recursion operators for the Kohn–Sham orbitals will frequently be well approximated by a "simple" form.

If one knows the recursion operators and the solutions to the Kohn–Sham equations for the elements of the highest occupied and lowest unoccupied sets of orbitals, then the Kohn–Sham density matrix (and hence the kinetic energy and electron density) can be constructed using the Christoffel–Darboux formula (Eq. 29). Iterative improvement to the self-consistent solution follows. If the computationally limiting step in the computational procedure is not the construction of the matrix recursion coefficients, such an approach could be competitive with the best existing linear-scaling algorithms for constructing the Kohn–Sham density matrix for large systems and similarly competitive with the more conventional orbital-based techniques used for small systems. If these hopes were realized, the chemically relevant and intuitively pleasing dependence on the frontier molecular orbitals would lead this author to favor a Christoffel–Darboux-based algorithm over the alternatives presently available.

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